

Metal Phthalocyanines Catalyzed Selective Organic Transformations: Recent Developments and Promising Future

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Achieving high levels of selectivity is one of the most daunting challenges of synthetic chemistry. In chemical synthesis, the term "selectivity" refers to the discrimination displayed by a reagent, when it reacts with two different reactants or functional groups. Highly selective reactions proceed with minimal reliance on protecting groups and contribute to both atom and step economy. Biological and synthetic systems operate somewhat differently when it comes to impose selectivity in chemical transformations. In nature, the biological catalysts, more particularly porphyrins such as cytochromes, are responsible for catalyzing oxidation-reduction processes and electron transfer reactions on which all forms of life are dependent. These enzymes are tailored towards a specific substrate and work with high levels of stereo-, regio- and chemoselectivity. However, high price, stability and bulk availability issues limit their practical utility.

Phthalocyanines (Pcs) have structural similarity with porphyrins and are very stable π -conjugated macrocyclic compounds that can form complexes with almost all metals and offer a high architectural flexibility in structure. Due to their greater stability than porphyrins, metal phthalocyanines (MPcs) attract great attention for their applications as catalysts for selective organic transformations including oxidation-reduction processes and electron transfer reactions.

Chauhan et al. have utilized CoPc for the selective reduction of flavones and isoflavones with sodium borohydride as reducing agent [1,2]. The mechanistic study revealed the involvement of electron transfer mechanism through the formation of hydridocobalt (III) complex. Our group employed phthalocyanine complexes of Fe, Co, Cu and Zn for chemo- and regio-selective reduction of nitroarenes to corresponding amines tolerating a large range of reducible functional groups such as acid, amide, ester, halogen, lactone, nitrile, *N*-benzyl, *O*-benzyl, hydroxy and heterocycles [3-5]. The mechanistic investigation on Co(II)Pc catalyzed reduction showed the formation of Co(I)Pc [4]. However, in another study on Co(II)Pc catalyzed chemo-selective reductive amination of carbonyl compounds using diphenylsilane as reducing agent, the involvement of a different mechanism was disclosed [6]. The Lewis acidic character of Co(II)Pc was found to be responsible for imine activation *via* a Lewis acid-base interaction. Ni(II)Pc showed excellent activity towards the selective reduction of carbonyl compounds [7]. High regio-selectivity in the reduction of dicarbonyl compounds was remarkable, which was observed for the first time.

Sorokin et al. have reported selective oxidations of phenols and condensed aromatics to quinones and alkynes to α,β -acetylenic ketones mediated by supported iron phthalocyanine complexes [8]. They reported a very different mechanistic features consistent with involvement of iron phthalocyanine centered species and free radicals as evidenced by ^{18}O labelling and kinetic isotope effect studies. In a bio-inspired approach, they further reported μ -nitrido iron phthalocyanine catalyzed oxidation of benzene for the formation of benzene oxide using H_2O_2 [9]. Contrary to this, replacing H_2O_2 with *t*-BuOOH resulted in industrially important selective oxidation of alkylaromatic compounds such as toluene or xylene to corresponding acids [10]. In addition to this, selective oxidation of various challenging substrates

such as cyclooctene, cyclohexene, styrene etc. have also been reported [11].

Some other examples of catalytic applications of MPcs include AlPc catalyzed cyanosilylation of aldehydes and ketones [12,13], PdPc catalyzed Suzuki and Heck coupling reactions [14] and CoPc catalyzed oxidation of alcohols and thiols [15]. MPcs have also been utilized in several photocatalytic transformations such as degradation of pollutants, oxidation of alkanes and alkenes, ene reaction etc. [16-18].

Although several catalyzed synthetic methodologies are being developed, controlling reaction selectivity still stands as one of the major challenges in organic synthesis. In this regards, these recent advances clearly evidenced the promising future of MPcs in catalyzing challenging organic transformations in which high selectivity is required. Currently, visible light absorbing photocatalysts are emerging as powerful tools in synthetic organic chemistry in which their electron/energy transfer potential is being utilized for sensitization of organic molecules. In this regard, MPC photosensitizers, which strongly absorb in the visible region and have long triplet lifetime, have great potential to be developed for efficient photocatalytic reactions.

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